On the Constitution of the Addition Compounds of Tertiary Phosphines and Carbon Disulfide

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The characteristic red addition compounds of the type $R_3P.CS_2$, formed from trialkylphosphines and carbon disulfide[1], were formulated by Jensen[2] as trialkylphosphoniodithioformates, $R_3\overset{+}{P}-CSS^-$, *i.a.* because they react with methyl iodide as do betaines, forming phosphonium salts of the type $[R_3\overset{+}{P}-CSSCH_3]I^-$. Issleib and Brack[3], however, reject this proposal and consider these compounds as loose addition compounds, mainly because the reaction between the phosphine and carbon disulfide is reversible, and the compounds — especially of the higher trialkylphosphines — are easily dissociated to trialkylphosphine and carbon disulfide. This is, however, not a convincing argument against the zwitterion formulation and we have therefore studied the infrared spectra of some of these compounds to obtain more conclusive evidence concerning their structure. The infrared spectra (Table 1) show none of the characteristic bands of carbon disulfide and it is therefore obvious that the conclusion of Issleib and Brack cannot be correct. The compounds also have very large dipole moments as required by the zwitterion formulation. This result is in accordance with a recent investigation by Margulis and Templeton[4] who have determined the structure of the triethylphosphine compound by X-ray diffraction and find that the shape of the molecule corresponds to the formula proposed by Jensen.

The main difference between the infrared spectra of the carbon disulfide adducts of trimethylphosphine (I), triethylphosphine (III), and tripropylphosphine (V) and the infrared spectra of the free phosphines (or co-ordination compounds of the phosphines) is a very strong band at 1042 cm^{-1}, 1065 cm^{-1} and 1050 cm^{-1}, respectively, in the infrared spectra of the three compounds. This band is assigned to the asymmetric vibration of the dithiocarboxylate ion, $-CSS^-$. No extensive investigation of this vibration has been published, but in the infrared spectra of a number of dithiocarboxylates we have similarly found a strong band near 1000 cm^{-1}. It should also be mentioned that a strong band has been found near 982 cm^{-1} in the spectra of a number of metal salts of dialkyldithiocarbamates[5] and between 1040 and 1080 cm^{-1} in the spectra of alkali metal xanthates[6].

The strong bands at 877 cm^{-1} and 886 cm^{-1}, respectively, in the spectra of the two phosphine compounds (I) and (III) are missing in the spectra of the phosphines but are found in the spectra of the corresponding selenium compounds (see the following paper) and thus cannot be due to the $-CSS$ grouping.

In the infrared spectra of the methyl iodide compounds (II, IV and VI) the above mentioned bands have disappeared and instead a strong band appears at 1087 cm^{-1}, 1091 cm^{-1} and 1080 cm^{-1}, respectively. This band is assigned to the $-CSSCH_3$ grouping and is probably characteristic of the $C=S$ bond.

Most of the other bands in the spectra of the four phosphine compounds correspond to bands in the spectra of the free phosphines and can be assigned to CH_3 and CH_2 vibrations with the exceptions of the bands between 650 cm^{-1} and 800 cm^{-1}, some of which are undoubtedly due to $P-C$ stretching. According to Hallmann[7] the $P-C$ symmetric stretching is found at 652 cm^{-1} and the asymmetric $P-C$ stretching band at 707 and 715 cm^{-1} in the spectrum of gaseous trimethylphosphine. The corresponding bands in the carbon disulfide adduct of trimethylphosphine are found at 679 cm^{-1} and 772 cm^{-1}. The assignment of the band at 772 cm^{-1} to asymmetric $P-C$ stretching is in accordance with the fact that a strong band occurs at nearly the same place in the compounds III and IV, in liquid triethylphosphine[8] and in complexes of triethylphosphine with nickel, cobalt and platinum halides, but is absent in the spectra of corresponding complexes with triethylarsine and triethylstibine[9].

Experimental. The compounds I, III, and V (Table 2) were obtained as red crystals by addition of carbon disulfide to a solution of the phosphine in ether. Yields almost quantitative. The compounds are insoluble in water, and the compounds I and III are only slightly soluble in most organic solvents (ether, carbon disulfide, carbon tetrachloride, benzene, etc.), except chloroform and hot ethanol, from which they can be recrystallised. The tripropylphos-

Table 1.

I. $(CH_3)_3\overset{+}{P}-CSS^-$	679 m, 772 m, 802 vw, 862 s, 870 s, 877 s, 957 vs, 968 vs, 979 sh, *1044 vs*, 1290 s, 1405 m, 1415 m, 2920 m, 2990 m.
II. $[(CH_3)_3\overset{+}{P}-CSSCH_3]I^-$	667 vw, 769 vw, 802 vw, 864 m, 878 w, 902 w, 959 sh, 967 vs, 992 s, *1087 s*, 1287 m, 1298 m, 1304 sh, 1400 w, 1417 w, 2880 w, 2955 m.
III. $(C_2H_5)_3\overset{+}{P}-CSS^-$	636 m, 723 m, 745 vs, 772 vs, 886 w, 983 m, 1015 s, 1044 s, *1065 vs*, 1240 w, 1259 w, 1380 w, 1393 w, 1405 m, 1417 w, 1451 m, 1458 m, 2905 m, 2945 m, 2975 m.
IV. $[(C_2H_5)_3\overset{+}{P}-CSSCH_3]I^-$	720 sh, 733 sh, 750 s, 777 s, 787 s, 902 m, 974 w, 981 w, 995 w, 1010 w, 1025 w, 1045 m, 1063 w, *1091 s*, 1230 vw, 1272 w, 1318vw 1407 m, 1452 m, 1465 m, 2880 s, 2925 w, 2985 w.
V. $(n\text{-}C_3H_7)_3\overset{+}{P}-CSS^-$	720 m, 770 w, 835 w, 900 vw, 1025 s sh, *1050* vs, 1075 s sh, 1225 w, 1340 vw, 1370 w, 1390 w, 1457 m, 2875 m, 2930 m, 2965 s.
VI. $[(n\text{-}C_3H_7)_3\overset{+}{P}-CSSCH_3]\ I^-$	720 m, 905 w, 1050 m, *1080 vs*, 1225 w, 1305 w, 1370 w, 1395 m, 1455 m, 2860 s, 2920 m, 2960 s.

phine derivative is rather soluble in organic solvents. In benzene and carbon tetrachloride solution it is rapidly dissociated into carbon disulfide and the phosphine as shown by a rapid change of the dark red colour of the solution to almost colourless. In carbon disulfide it dissolved with a dark red colour; its dipole moment in this solvent was found to be 8.0 D. The methyl and ethyl compounds were not soluble enough in carbon disulfide to allow a measurement of their dipole moments.

The methyl iodide derivatives II, IV, and VI (Table 2) were prepared by addition of the equivalent amount of methyl iodide to chloroform solutions of the compounds I, III, or V, and precipitation by addition of pentane. The iodides have a more intense red colour than the parent compounds. They are almost insoluble in nonpolar organic solvents but easily soluble in ethanol and, in contrast to compounds I, III, and V, are also soluble in water (with red colour). The compounds are changed rapidly and it has not been possible to obtain wholly satisfactory analyses.

The infra-red spectra were recorded on a Perkin Elmer model 21 spectrophotometer equipped with NaCl-prism, the KBr-dics technique being used.

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Table 2.

	M.p., °C		Found		Calc.	
			C	H	C	H
I. $(CH_3)_3PCS_2$[1]	158	(subl.)	31.70	5.63	31.56	5.96
II. $[(CH_3)_3PCSSCH_3]I$	150	(decomp.)	21.75	4.87	22.91	4.61
III. $(C_2H_5)_3PCS_2$[1,11,12,13]	121–22	(subl.)	43.55	7.99	43.25	7.78
IV. $[(C_2H_5)_3PCSSCH_3]I$[10]	96–97	(decomp.)	28.80	5.94	28.55	5.39
V. $(n\text{-}C_3H_7)_3PCS_2$[14]	107–08	(subl.)	50.55	9.09	50.81	8.96
VI. $[(n\text{-}C_3H_7)_3PCSSCH_3]I$	77–79	(decomp.)	34.85	6.95	34.92	6.39

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